



Quantitative outgassing study of photosensitive films upon irradiation at 13.5 and 6.7 nm

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We characterized outgassed species and quantify the amount of outgassing from photosensitive films upon irradiation at 13.5 and 6.7 nm with a quadrupole mass spectrometer (QMS). A benchmark comparison revealed that absolute outgassing rates of polymethyl methacrylate (PMMA) and polystyrene (PS)/t-butylacrylate (tBA) copolymer films with or without photoacid generator determined by this work were consistent with values provided by CNSE or IMEC groups. Thus, we have effectively demonstrated that the Taiwanese facility is capable of evaluating absolute resist outgassing rates, making it one of limited facilities worldwide for evaluating EUV resist outgassing. Furthermore, we measured the dependence of outgassing on film thicknesses and polymeric structures with PMMA and two DuPont's EUV model resists at 193 and 103.3 nm (out-of-band, OOB), 13.5 and 6.7 nm. This work was conducted at the BL04B1-Seya and BL08A1-LSGM beamline of National Synchrotron Radiation Research Center in Taiwan.

Introduction

In our previous study [1], we have successfully benchmarked absolute quantities of resist outgassing upon 13.5 nm irradiation to those reported by Denbeaux's group at University of Albany financially supported by Sematech [2] and by Pollentier's group at IMEC [3], as listed in the following table.

Sample	Thickness (nm)	Outgassing rate, molecules cm ⁻² s ⁻¹				Previous works
		This work		Scaled to 10 mW cm ⁻²		
		13-200 nm ²	35-200 nm ² (excluding 44)	13-200 nm ²	45-200 nm ²	
PMMA	125	(2.2 ± 0.5) × 10 ¹⁵	(2.1 ± 0.9) × 10 ¹⁵			
	100	2.3 × 10 ¹⁵	1.4 × 10 ¹⁵			(3.3 ± 0.5) × 10 ¹⁶
	80	2.3 × 10 ¹⁵	2.5 × 10 ¹⁵			
RRR	125	8.9 × 10 ¹⁴	5.4 × 10 ¹⁴			(3.2, 7.5) × 10 ¹⁶
	100	8.4 × 10 ¹⁴	5.4 × 10 ¹⁴			
UL-SiOCH	30			4.3 × 10 ¹⁴	7.2 × 10 ¹³	4.1 × 10 ¹⁶ 1.4 × 10 ¹⁵
UL-CHO-1	15	2.2 × 10 ¹⁴	2.3 × 10 ¹³	6.5 × 10 ¹⁴		
UL-CHO-2	15	2.7 × 10 ¹³	2.7 × 10 ¹³	1.5 × 10 ¹⁴	1.6 × 10 ¹³	
				1.8 × 10 ¹²	1.8 × 10 ¹²	

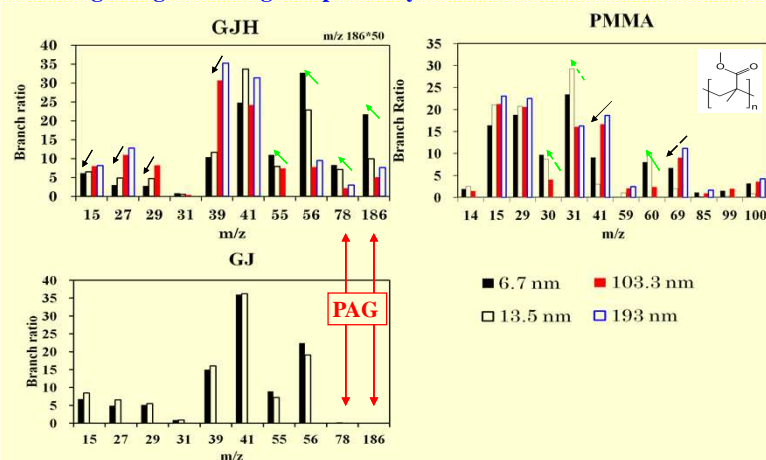
Resist outgassing up DUV OoB, EUV at 13.5 nm and beyond EUV (BEUV) at 6.7 nm are characterized here by the quadrupole mass spectrometer (QMS) method.

Experimental

- Light source:** 6.7 and 13.5 nm light from BL08A beamline, and OoB at 103.3 and 193 nm from BL04B beamline of NSRRC.
- Equipment:** QMS
- Photosensitive film:**
 - PMMA (film thickness: 130 and 60 nm)
 - Polystyrene (61 wt%) + tertbutyl acrylate (39 wt%), w/ or w/o 5 wt% PAG((C₆H₅)₃SC₄F₉SO₃), (film thickness: 120 and 70 nm) denoted here as GJH and GJ, respectively.

Results

Outgassing: wavelength dependency



-Wavelength effect on PMMA

- fragmentation pairs: m/z 69 – 31(30) = C₄H_{5.4}O – CH₃O
- m/z 59(60) – 41 = HC(O)OCH₃ – C₃H₅

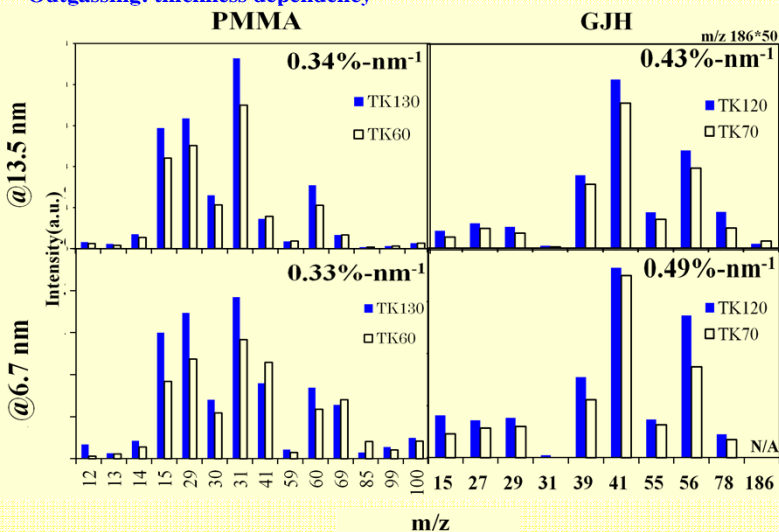
-Wavelength effect on PS-tBA:

- fragmentation partition within the deprotection group.

-Wavelength effect on PAG ((C₆H₅)₃SC₄F₉SO₃):

- PAG outgassing is in the greatest extent by BEUV.

Outgassing: thickness dependency



-Thickness dependency is calculated by:

$$\text{Thickness Dependency (\% - nm}^{-1}\text{)} = \frac{\left(\frac{\Delta \text{Intensity}}{\text{Mean Intensity}} \right)}{\Delta \text{Thickness}}$$

-Similar thickness dependency found for PMMA and GJH at 13.5 and 6.7 nm, in the order of 0.3-0.5%·nm⁻¹.

-Thickness effect assessment: For example of two 60 and 130 nm films, the thickness dependency would be about 0.4%·nm⁻¹ × ΔT ~24%.

Summary

The outgassing evaluation system at NSRRC in Taiwan is one of limited facilities worldwide capable of this type of research. We have measured outgassing from PMMA, GJ and GJH upon OOB, EUV and BEUV irradiation, and present here that the dependency of outgassing on wavelengths, film thicknesses, compositions, and PAGs. We concluded: (1) Similar outgassed species but their relative abundance evolve as a function of light wavelengths. (2) The 6.7 nm light gives off the most amount of PAG fragment. (3) The extent of thickness dependency is ~0.3 to 0.5%·nm⁻¹ for the samples investigated here both by EUV and BEUV light.

Reference

- [1] Grace H. Ho, et al., *Journal of Vacuum Science and Technology B*, 2012.
- [2] K. R. Dean et al., *Proc. SPIE* 6519, 65191P (2007).
- [3] A. O. Antoe, C. Mbanaso, Y.-J. Fan, L. Yankulin, R. Garg, P. Thomas, G. Denbeaux, E. C. Piscani, and A. F. Wuest, *Proc. SPIE* 7271, 727126 (2009).

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